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EXECUTIVE SUMMARY

DETERMINATION OF TRITIUM ACTIVITY IN OIL SAMPLES BY LIQUID SCINTILLATION COUNTING

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The determination of tritium in different oil samples is required for transportation and disposal purposes. Many of these oils have degraded in service and have become colored. Some of the waste oils may also be mixed with other waste solvents. This results in samples which are difficult to analyze for tritium by liquid scintillation counting due their color and luminescent nature. A simple procedure for a reliable determination of tritium in these oil samples was standardized and is presented in this report.

job	file	date	report no.
33-090	830.6	April 12, 1990	90-68-K

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To: Dr. D. Mills
Director of Research

DETERMINATION OF TRITIUM ACTIVITY IN OIL SAMPLES BY LIQUID SCINTILLATION COUNTING

S.P. Sood and D.Kos

A simple procedure for the determination of tritium activity in colored oil samples using liquid scintillation counting has been standardized. The recommended procedure permits scintillation counting of non-luminescent oils with activities >10 nCi/kg. Tritium in highly colored or luminescent oil samples with activity <500 nCi/kg cannot determined by this method and must be combusted in a sample oxidizer prior to analysis.

1.0 INTRODUCTION

The determination of tritium in different oil samples is required for transportation and disposal purposes. Many of these oils have been in service for some time and have degraded and become colored. Some of the waste oils may also be mixed with other waste solvents. This results in colored, luminescent (chemiluminescence and/or photoluminescence) samples that show large quenching (chemical as well color quench) during liquid scintillation counting for tritium. Such samples cannot be reliably counted using normal calibration curves /1/. Also many oil samples are viscous and cannot be pipetted easily for taking a known aliquot. A simple standard procedure to deal with these difficult samples was therefore required to produce reliable tritium results. This report summarizes the efforts to standardize such a procedure by applying it to different field samples received by the Analytical Services Section for tritium analysis. The recommended procedure is appended.

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2.0 EXPERIMENTAL PROCEDURE

2.1 Calibration of Liquid Scintillation Counter

Ten samples, each containing the same amount of tritium (57.7 nCi) and 15 mL of Monophase liquid scintillation cocktail, were prepared and counted on a Packard Series 2000 Liquid Scintillation Counter (LSC). This was done to verify that the count rates of all the samples were the same within acceptable statistical variations. A set of quenched standards was then prepared by adding increasing amounts of highly colored oil, initially in steps of 0.1 g and then later in larger amounts, to produce a range of quenched samples. These standards (containing both chemical as well as color quench) were dark adapted for 20 minutes and used to prepare a calibration curve with window settings of 0 -18.6 keV and 20 - 2000 keV. The calibration curve for the first window is used to measure the activity of the tritium in oil.

2.2 Counting Efficiency Calibration Checks

Two samples were prepared, each containing 15 mL of Monophase liquid scintillation cocktail and 115.4 nCi of tritium. To one of the samples 0.5 g of a known inactive light oil and to the other sample 0.2 g of an uncontaminated dark oil was added. Both samples were dark adapted for 20 minutes. and counted to verify the validity of the counting efficiency curve being used by the LSC for the tritium in oil analysis.

2.3 Method Verification by Standard Addition

A 1.0 g sample of a colored oil containing tritium was mixed with 15 mL of Monophase, dark adapted and counted. An aliquot of a certified tritium standard (50 uL) was added to the sample and it was recounted. Three more aliquots were then added and the sample recounted after each addition.

2.4 Method Verification by Combustion in a Sample Oxidizer

Several very dark colored waste oil samples were available that had previously had their tritium contents measured elswhere. These samples were analyzed by the present method and compared with the field values. Subsamples of four of them were combusted in a Packard TRICARB Sample Oxidizer to verify the data.

3.0 RESULTS AND DISCUSSION

3.1 Efficiency of Tritium Counting

The tritium efficiency curve for the set of quenched oil standards is shown in Figures 1. The counting efficiency for the 0 - 18.6 keV window was in the range of 56 to less than 20%. A dark adaptation period of 20 minutes was sufficient to eliminate the luminescence in samples to which up to 1 g of new oil had been added. Samples containing larger quantities of the oil

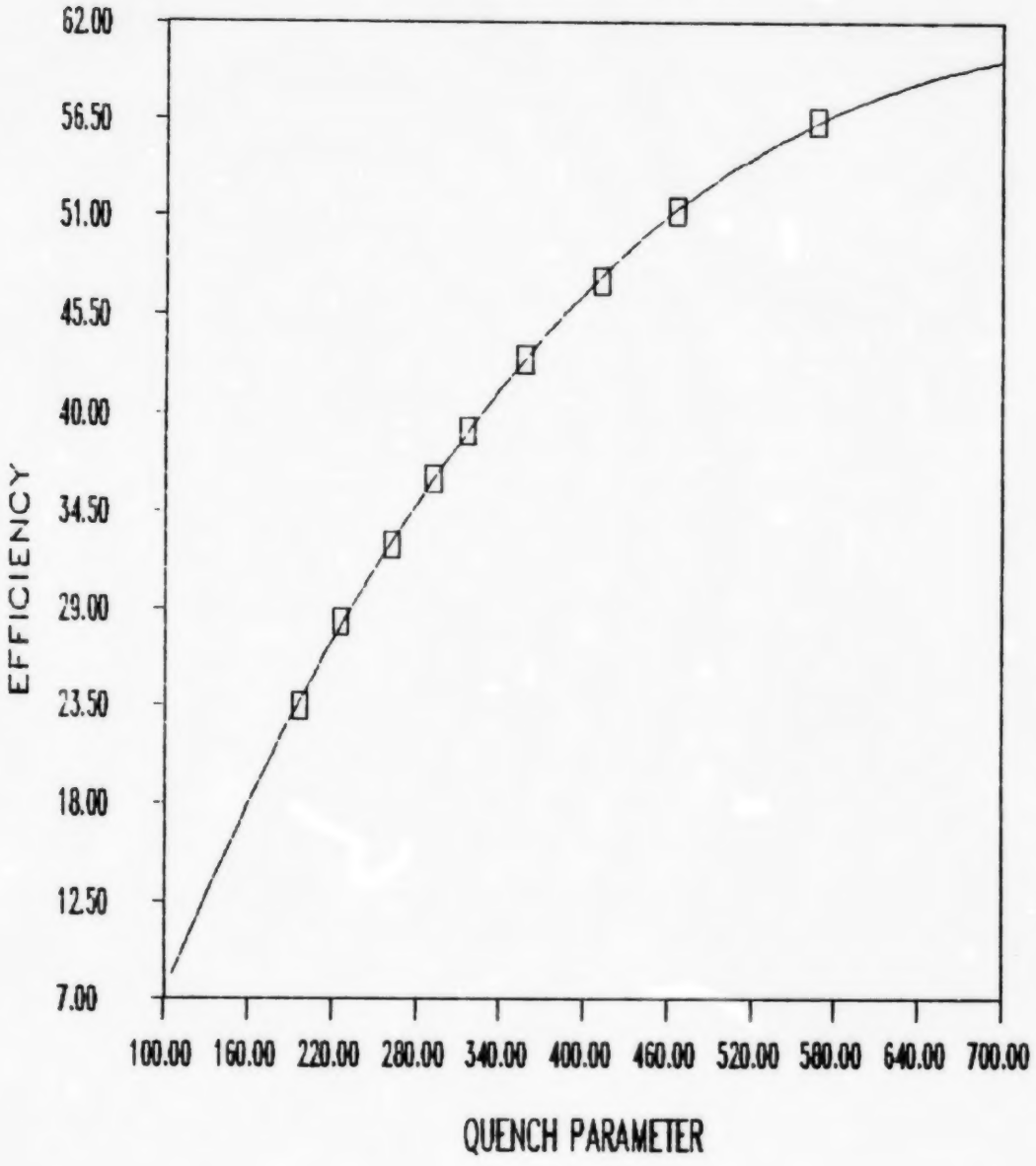
COUNTING EFFICIENCY FOR H-3 IN OIL
62.00
56.50
51.00
45.50
40.00
34.50
29.00
23.50
18.00
12.50
7.00
EFFICIENCY
100.00
160.00
220.00
280.00
340.00
400.00
460.00
520.00
580.00
640.00
700.00
QUENCH PARAMETER

FIGURE 1

(up to 2 g) showed some luminescence (1-2 %), even after a dark adaptation for 2 hours. However, the LSC was able to correct for this effect during the calibration to produce the efficiency curve. Less than 1% of the counts recorded in the 0 - 18.6 keV window were registered in the 20 to 2000 keV window. These are mainly due to the random summation of tritium pulses (at the large count rates used for calibration purposes) to produce a pulse of apparently higher energy. Large numbers of counts in this channel indicate the presence of other beta emitters in the sample, which would interfere in the determination of true tritium content of the oil sample.

3.2 Verification of the Tritium Counting Efficiency

The results of counting a known tritium activity mixed with oil are shown in Table 1. The sample with the dark oil still showed some residual luminescence. However, the automatic correction routine in the LSC made a reasonable correction for this and the results demonstrate that use of the calibration curve produces an acceptable value for tritium activity.

Table 1

Sample	Activity Taken (nCi)	Activity Measured after the Addition of Oil (nCi)
Light Oil 0.5 g	115.4	115 ± 4
Dark Oil 0.2 g	115.4	113 ± 4

3.3 Method Verification by Standard Addition

The results of counting a spiked oil sample are listed in Table 2, along with the measured activity of the un-spiked sample. A plot of added activity vs the measured is shown in Figure 2. The extrapolated line intersects the X-axis at 57.5 nCi. This agrees well with the measured value of 58 ± 1 nCi. The slope of the line is 1.012, showing that essentially all of the added tritium was recovered. With increasing addition of aqueous standard there is increased quench in the sample. The LSC was able to correct for this quite satisfactorily, resulting in near unity slope. It also demonstrates that samples containing up to 200 uL water per gram of oil can be counted reliably.

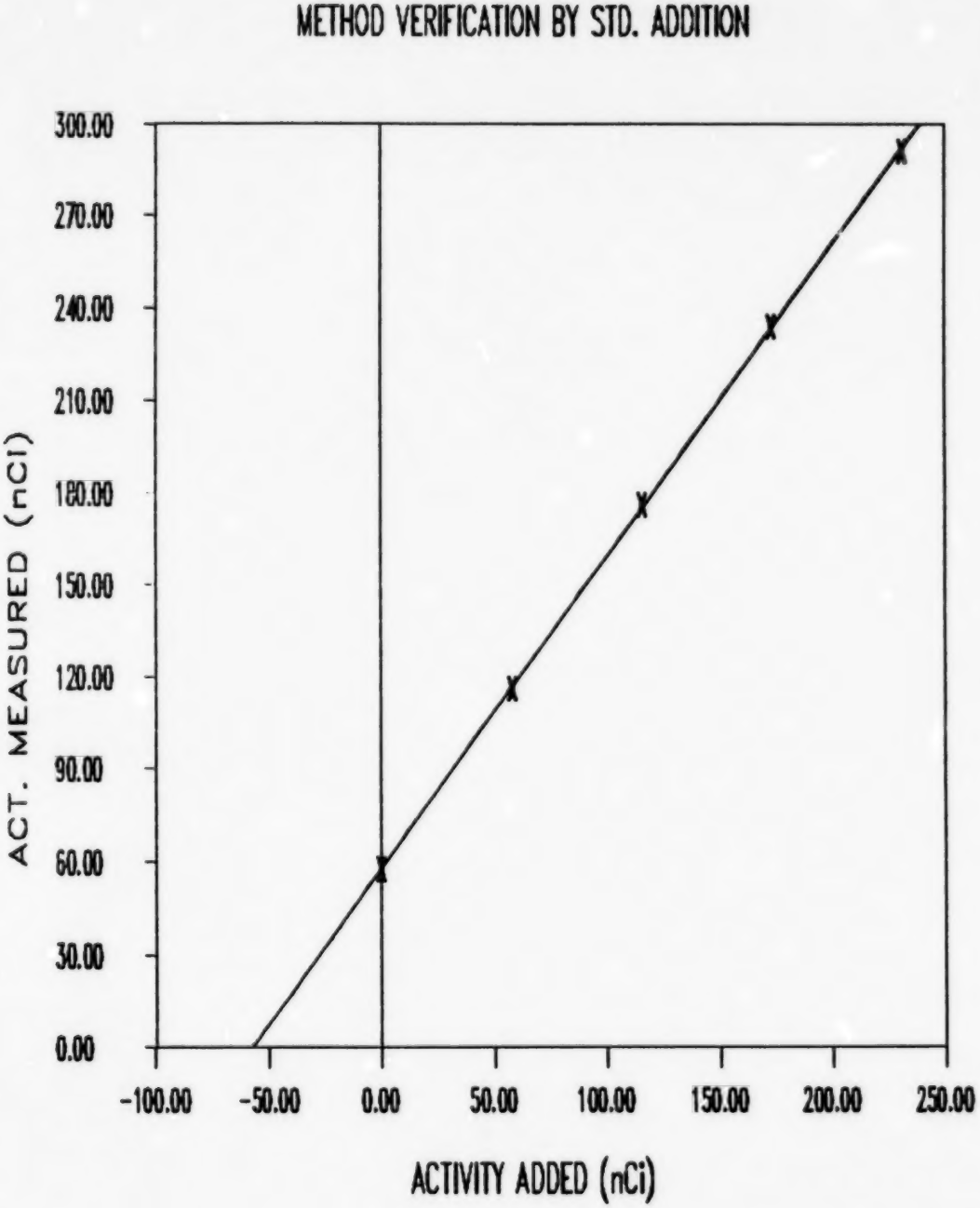
METHOD VERIFICATION BY STD. ADDITION
ACT. MEASURED (nCi)
300.00
270.00
240.00
210.00
180.00
150.00
120.00
90.00
60.00
30.00
0.00
-100.00
-50.00
0.00
50.00
100.00
150.00
200.00
250.00
ACTIVITY ADDED (nCi)

FIGURE 2

Table 2

Sample	Activity Added (nCi)	Activity Measured (nCi)	Activity Recovered (nCi)
Oil sample (1.0 g)	0	58 ± 2	-
	57.7	116 ± 3	58 ± 3
	115.4	176 ± 4	118 ± 4
	173.1	234 ± 5	176 ± 5
	230.8	291 ± 6	233 ± 6

3.4 Method Verification by Combustion in a Sample Oxidizer

The experimental data generated by the two techniques used at Chemical Research, along with the field data supplied with the samples, are listed in Table 3.

Table 3

	Field Data	Research Data (H-3 Activity)	
Sample #	Activity (uCi/kg)	By Oxidizer (uCi/kg)	By This Method (uCi/kg)
1	66	3.9 ± 0.3	3.7 ± 0.3
2*	155	8 ± 2	8 ± 2
3	37	94 ± 5	94 ± 5
4	457	142 ± 8	172 ± 10

* Sample required a second dilution before it could be counted satisfactorily by the LSC.

Large discrepancies exist between the field data and those generated by the present LSC method. The results obtained by sample oxidation using the TRICARB Sample Oxizer (which destroys the matrix and hence is interference free) generally agree well with those obtained by the present method, although there was a 20% difference for sample #4. Little information is

available about the field measurement technique, but it is clear that those results cannot be reproduced at Chemical Research.

3.5 Minimum Detectable Activity for Tritium Determination in Oil Samples by Liquid Scintillation Counting

A 1 g aliquot of an inactive oil sample was counted for 10 minutes and the Minimum Detectable Activity (MDA) for the above procedure was calculated from this single background count, using a standard procedure /2/ as follows:

$$MDA = \frac{4.65 \times \text{SQRT(background count)} \times 1000}{10 \times 2.22 \times \text{counting efficiency}} = 10 \text{ nCi/kg}$$

4.0 CONCLUSIONS

The tritium activity of a waste oil sample can be measured reliably by LSC when the instrument is calibrated and the sample prepared by the proposed method.

An estimate of the amount of other beta emitters present in the sample can be made from the activity found in the window set at 20 to 2000 keV. Large quantities of these will interfere in the tritium determination. Separate calibrations are required to handle such samples.

Under optimum conditions, the MDA of this procedure (1 g sample, 10 minutes count and the Series 2000 LSC) is 10 nCi/kg. Higher MDA's ($\sim$500 nCi/kg) are expected when very dark and dirty oils are analyzed using other liquid scintillation counters having higher backgrounds.

Samples which cannot be counted using LSC because of high quench or luminescence, even after a second dilution, must be combusted in a sample oxidizer to obtain their tritium contents.

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REFERENCES

1. M. Benotto, CANBERRA PACARD CANADA, Private Communication.

2. L.A. Currie, "Limits of Qualitative detection and Quantitative Determination -Application to Radiochemistry", Analytical Chemistry, 40, 586(1968).

APPENDIX

ANALYTICAL PROCEDURE

DETERMINATION OF TRITIUM ACTIVITY IN OIL SAMPLES USING LIQUID SCINTILLATION COUNTING

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DETERMINATION OF TRITIUM ACTIVITY IN OIL SAMPLES USING LIQUID SCINTILLATION COUNTING

EQUIPMENT AND SUPPLIES

- A clean laboratory working area containing a fume hood and an analytical balance.
- Various reagents and chemicals as detailed in a separate section entitled "REAGENTS AND SOLUTIONS".
- Glassware and other laboratory ware as described in a separate section entitled "APPARATUS".
- Packard Series 2000 Liquid Scintillation Counter.
- Liquid scintillation counting supplies and radioactive standards solutions.

STANDARDIZATION

- Calibrate the liquid scintillation counter for tritium counting by determining the efficiency vs quench curve using a set of especillay prepared tritium quenched standards. Latter being prepared by using an inactive dark colored oil as a quenching agent.

1. OUTLINE OF THE METHOD

The "as received" oil sample is visually inspected for homogeneity and if no other phases are present, it is well mixed. An aliquot (up to 1 g if the oil color is light or less for darker oils) is mixed with a known amount of liquid scintillation cocktail and counted after dark adaptation for 20 minutes. If the quenching of the resultant solution is such that the counting efficiency is less than 20%, a further 10:1 dilution of this cocktail-oil mix is made with fresh cocktail and recounted. Samples with high luminescence should also be diluted before final counting. In case the counting efficiency or luminescence of diluted sample is still unacceptable, the oil needs to be combusted in a Tricarb sample oxidizer for tritium determination. Triplicate measurements are made to assure the reliability of the results. A poor agreement in the replicate counts requires repeat analysis with much larger sample size.

2. INTERFERENCES

The procedure is designed to reduce the uncertainty caused by the presence of tritiated water mist and color quench of the sample. The presence of non-tritium beta activity in the sample is indicated by the large number of counts in the window at 20 to 2000 keV (>1% than those in the tritium window). These are normally determined by other techniques such as gamma spectroscopy. Other pure beta emitters are not determined unless the system is specifically calibrated for them and hence interfere in the analysis. Luminescence in the sample should be eliminated/reduced by dark adaptation for at least 20 minutes before counting. The counter will correct for some luminescence, however, high luminescence (caused by chemiluminescence or excess photoluminescence) will interfere in the determination.

3. CONCENTRATION RANGE AND MINIMUM DETECTABLE ACTIVITY

The lower limit of detection depends on the color and luminescence properties of the sample (and therefore the dilution required) and the system background. For a counting period of 10 minutes, 1 g sample and a low background liquid scintillation counter a minimum detectable activity of about 10 nCi/kg has been obtained. No upper limit is assigned to this technique as the sample can be diluted (with an inert solvent such as dioxane or liquid scintillation cocktail) to bring the activity level to one which can easily be counted.

4. PRECISION AND ACCURACY

For oil samples containing low tritium activity, the precision of the method is controlled by the amount of sample which can be counted and the counting statistics. For samples containing only tritium at >1 uCi/kg of tritium level a precision of +/- 10% has been calculated for

a 95% confidence level. The accuracy of the method was determined by analyzing oil samples containing only tritium and spiked by standard tritiated water. The measured value compared acceptably well with the added spikes. The method was also verified by the oxidation of sub-samples in a TRICARB Sample Oxidizer.

5. REAGENTS AND SOLUTIONS

- A Std. tritium solution (nominal 1.1 uCi/g).
- A highly colored inactive oil.

6. APPARATUS

6.1	Pyrex beakers	500 mL capacity
6.2	Oxford Pipette	10 mL capacity
6.3	Eppendorf pipette	1 mL capacity
6.4	Liquid Scintillation Cocktail dispenser	Fisher
6.5	Balance	

7. CALIBRATION OF THE LIQUID SCINTILLATION COUNTER

Ten samples, each containing 50 uL of certified standard tritium solution and 15 mL of Monophase, are prepared and counted on a Packard Series 2000 Liquid Scintillation Counter. This is done to verify that the count rates of all the samples are the same within acceptable statistical variations. A set of quenched standards is then prepared by adding increasing amounts of highly colored oil, initially in steps of 0.1 g and then later in larger amounts, to each of the above samples and make up the weight to 15 g with Monophase. The liquid scintillation counter is calibrated for tritium using these quench standards after 20 minutes of dark adaptation. The calibration curve is recorded and used to measure the tritium activity of the oil. A window set between 20 keV and 2000 keV is used to indicate the presence of other radionuclides.

8. PROCEDURE

Visually inspect the oil sample for homogeneity and color. If there is no other phase present mix the sample well and take a subsample of 0.1 g to 1 g depending on the oil color in to a liquid scintillation vial. If more than one phase (oil, water and/or sludge) is present, subsample the oil layer carefully making sure not to take any aqueous

layer. Add 15 mL of liquid scintillation cocktail to the vial and mix and reweigh. Dark adapt the vial for at least 20 minutes in the LSC and then count. Check the efficiency (by the quench) and the count rate of the sample if the efficiency is < 20% or the count rate is too high (over 500,000 counts), take 1 to 2 g of the sample from the vial and dilute it with more cocktail and recount. If the sample luminescence is large then dark adapt it for some more time. If this does not reduce the luminescence then dilute as above and recount. If the counting efficiency or the luminescence of the diluted sample is still unacceptable then the oil must be combusted in a Tricarb sample oxidizer for analysis. Repeat the above analysis twice more to verify the homogeneity of the sample. If large differences are observed in the triplicate results (generally indicating a presence of tritiated water mist), repeat the analysis by taking a larger subsample as follows:

To a 1 to 10 g subsample add a known weight of liquid scintillation cocktail and mix well. Count an appropriate aliquot from this solution as before.

9. CALCULATIONS

9.1 The activity of the subsample is given by the liquid scintillation counter output.

9.2 Activity of the oil sample can be calculated from the subsample weight and any known dilution factors.

9.3 The Minimum Detectable Activity (nCi/kg) is determined as follows:

$$MDA = \frac{4.65 \times \sqrt{\text{background count}}}{\text{Sample Wt.(g)} \times 2.22 \times \text{Eff.} \times \text{Counting Time}}$$

9.4 Standard deviation in the measurement is also given by the liquid scintillation counter.